Experimental Studies of Glucose Influence on Polyvinyl Alcohol (PVA) Foils

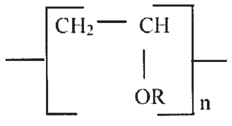
IRINA DUMITRAŞCU[1], LEONAŞ DUMITRAŞCU[1], MAGDALENA AFLORI[2], MIOARA DROBOTĂ[2], IULIANA STOICA[2], DANA-ORTANSA DOROHOI[1]
[1]"Al. I. Cuza" University, Faculty of Physics,11A, Carol I Bdv., 700506, Iaşi, Romania
[2]"Petru Poni" Institute of Macromolecular Chemistry, 41A, Grigore Ghica Vodă Drive, 700487, Iasi, Romania

This article presents the experimental results regarding the glucose influence on poly (vinyl alcohol) (PVA) films. The results of infrared spectroscopy (FTIR), atomic force microscopy (AFM) and X-ray diffraction (XRD) measurements revealed the surface and structural changes induced by increasing the glucose concentration.

Keywords: PVA, AFM, XRD, FTIR

Poly (vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer. It is the largest volume synthetic polymer produced in the world [1]. The excellent chemical resistance, physical properties, and complete biodegradability of PVA polymers have led to their broad practical applications including: polymeric membranes, nanostructured composites materials, nanofibers [2 - 4] optoelectronic and photonic devices [5, 6]. Polyvinyl alcohol has excellent film forming, emulsifying, and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength, flexibility, as well as high oxygen and aroma barrier. However these properties are dependent on humidity, in other words, with higher humidity more water is absorbed. The water, which acts as a plasticizer, will then reduce the PVA film tensile strength, but increase its elongation and tear strength.

The structure of poly (vinyl alcohol) (partially hydrolyzed) is given in figure 1.



$$-\left[CH_2 - \underset{OR}{CH} \right]_n-$$

where R = H or $COCH_3$

Fig. 1. PVA

PVA has a melting point of 230°C and 180 – 190°C for the fully hydrolyzed and partially hydrolyzed grades, respectively. It decomposes rapidly above 200°C as it can undergo spyrolysis at high temperatures. PVA is an atactic material [7] but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it.

The study of the induced anisotropy in PVA foils containing rod-like molecules [8-13] represents an important field to be studied.

Glucose (fig. 2) is an organic component of the human body, being distributed in all cells and biologic fluids, excepting ureea. Glucose is the main human source of energy. In medicine, the glucose is mainly used as aqueous solutions for perfusions. The solutions with a glucose content higher than 5% (10, 20, 33, 40 %) are hipertonique and are used as osmothique diuretics (realises tissue dewatering, useful in edema). In order to avoid the negative effects of hyperglycemia, the insuline is added to each glucose perfusion.

PVA is a degradable polymer, used in medical purposes. Many compounds included in PVA matrices are rejected begining with a given concentration. This is the case of glucose oxydaze in PVA [14]. PVA is used on a large scale, to realize glucose biosensors [15,16].

The aim of this study was to analyse the glucose influence on the transparency, optical properties and surface properties of the PVA foils obtained from PVA gels with variable content in glucose.

Materials and Sample Preparation

The studied samples were prepared as films by boiling the solution of PVA and glucose in distilled water into a marine bath for a long time (about 10 hours) and cooling them in a plate glass surface. The samples composition is given in table 1.

Table 1
COMPOSITION OF STUDIED SAMPLES

Sample	PVA	Glucose
pure APV	40 g	0 g
75 % APV and 25 % glucose	30 g	10 g
67% APV – 33 % glucose	20 g	10 g
50% APV – 50% glucose	20 g	20 g

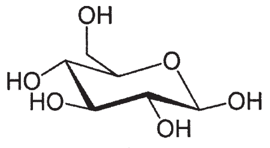


Fig. 2. Glucose

Experimental part

FTIR measurements

The modification in the PVA structure was examined by FTIR-ATR spectroscopy in the range 600-1800 cm^{-1}. The spectra were recorded on a BRUKER VERTEX70 spectrometer at a resolution of 2 cm^{-1} at incidence angle of 45°. The signal-to noise ratio was improved by co adding 128 scans per spectrum. Peak height measurements were performed with the spectral analysis software (Opus 5).

PVA absorbance bands are as follows: 3292 ν(O-H); 2938, 2905 ν(CH);1450 δ(C-H + O-H); 1419 δ(CH2); 1373 γ(CH2); 1321 δ (C-H + O-H); 1235 γ(C-H); 1142 ν (C-O + C-C); 1085 ν(C-OH) + δ(O-H); 913 γ(CH$_2$); 844 ν(C-C) The C-O stretching mode of vinyl alcohol units is at1085 ν (C-OH) + δ(O-H)). Very important is the effect of crystallinity of samples on this band, especially in the cases of PVA C-O-C stretching band, consistent with the lower amount of hydroxyl-carbonyl hydrogen bonding. The C-C-C stretching band (1142 cm^{-1}) is related to the crystalline regions of PVA, this sharp band is only present for the samples with higher hydrolysis degrees.

For the spectrum of D-glucose, the absorbance peaks 837 and 622 cm^{-1} are assigned to C-H vibrations, the peaks in the range of 1200-1460 cm^{-1}, 1250 cm^{-1} may be due to the C-O stretch in the C-OH group as well as to the C-C stretch in the carbohydrate structure. The peaks δ (C-O-H) 1016 cm^{-1} and the peak ν (CO) 1050 cm^{-1} and ν(C-C) 912 cm^{-1} could be assigned to the carbohydrate structure.

After the treatment, a lot of functional groups are still present and the appearance of the band at 1031 cm^{-1} may be due to the ν(C-O) stretch in the C-OH group as well as the C-C stretch in the carbohydrate structure corresponding to glucose compound. This band increases in intensity when the glucose concentration increases and the peak at 1081 cm^{-1} corresponding PVA compound decreases with process evolution (when glucose compound is increasing).

The ratio of the 1081 to 1032 cm^{-1} bands intensities decreased (fig. 3) when the glucose concentration in the PVA gel increased, showing that, when the foils are made, a part of the glucose crystalizes in the exterior and at the ends of the foils. The foil becomes nonhomogeneous with zones with conglomerates of glucose.

Results and discussions

AFM measurements

AFM measurements are performed in air at room temperature, in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NTMDT, Russia) with commercially available NSG10/Au Silicon cantilevers. The manufacturer's values for the probe tip radius are 10 nm, and the typical force constant is 11.5 N/m. In the tapping mode, the cantilever is oscillated at a frequency of 254.244 kHz. Representative scans of the film surface were obtained for each sample. The Root Mean Square (RMS) roughness parameter, Sq, which is the root mean square of the surface departures from the mean plane within the sampling area, is extracted from the Nova software provided (1):

$$S_q = \sqrt{\frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M} z^2\left(x_i x_j\right)} \qquad (1)$$

where M is the number of columns in the surface and N is the number of rows in the surface. Off-line image analysis on quantification of surface properties using the surface roughness parameter is obtained (fig. 4). The Root Mean Square increased with increasing of glucose percent (table 2).

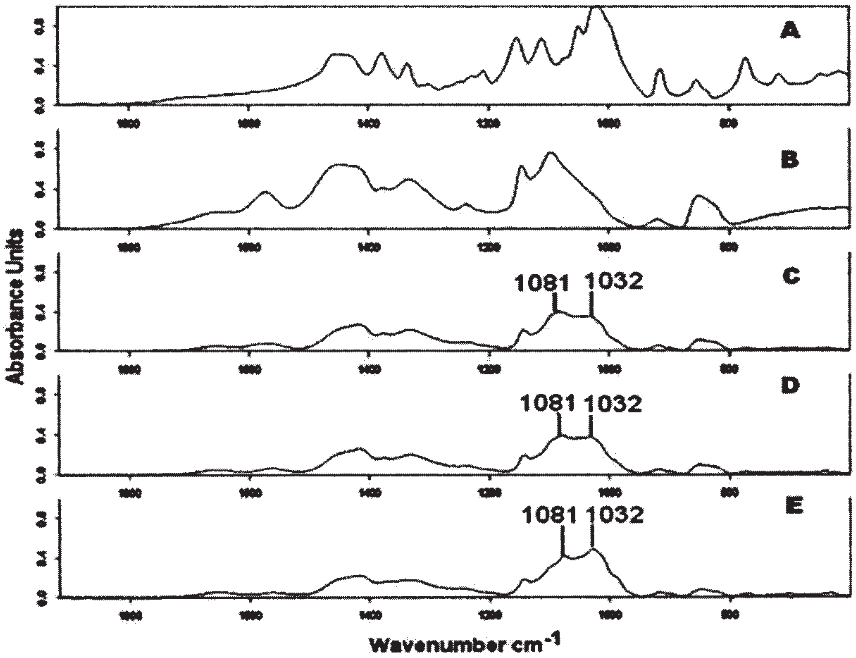


Fig. 3. ATR-IR spectra of PVA films unpurified with glucose: A) Virgin PVA; B) Virgin Glucose; C) 30 % PVA + 10% Glucose; D) 20% PVA + 10% Glucose; E) 20% PVA +20% Glucose

Table 2

ROOT MEAN SQUARE INCREASING WITH THE GLUCOSE CONTENT IN PVA FILMS

Sample	Root Mean Square, Sq (nm)
pure PVA	5,77
75 % APV – 25 % glucose	3,19
66,6 % APV – 33,3 % glucose	8,05
50% APV – 50% glucose	12,81

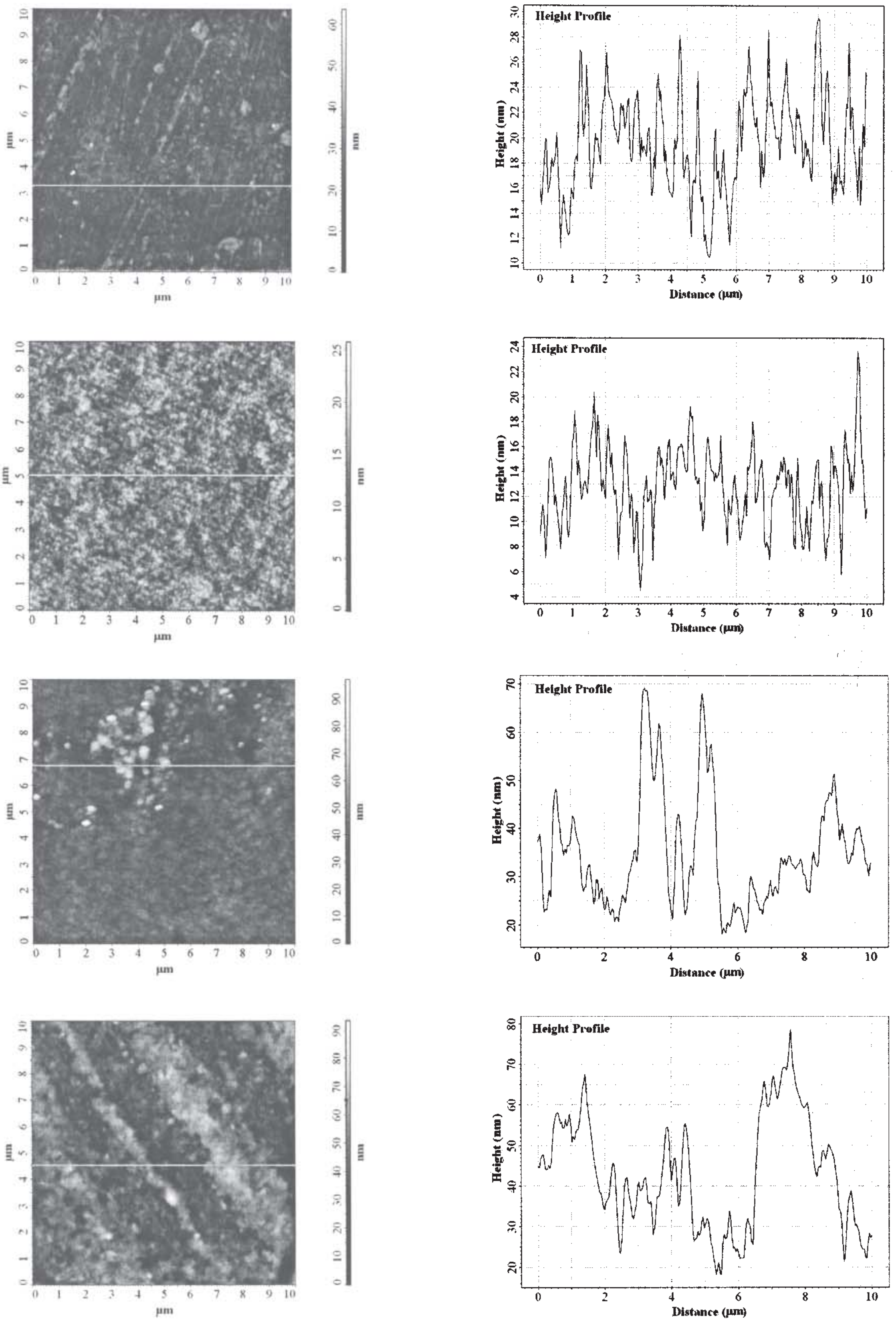


Fig. 4. AFM images and height profile for: a) Pure PVA; b) 75 % PVA - 25 % glucose; c) 66%; PVA - 33% glucose; d) 50 % PVA - 50 % glucose

XRD measurements

X-ray diffraction (XRD) patterns were recorded with an D8 Advance Bruker AXS. The X rays were generated using a CuKα source with an emission current of 36 mA and a voltage of 30 kV. Scans were collected over the 2θ = 2 - 70° range using a step size of 0.01° and a count time of 0,5 s/step. The semi-quantitative analysis was performed with an EVA soft from DiffracPlus package and a ICDD-PDF2 database based on the patterns' relative heights. The crystallographic system is monoclinic with unit. Cell parameters: a = 7.81; b = 2. 52; c = 5.51.

The crystallinity degree decreases with increasing of glucose percent (fig.5).

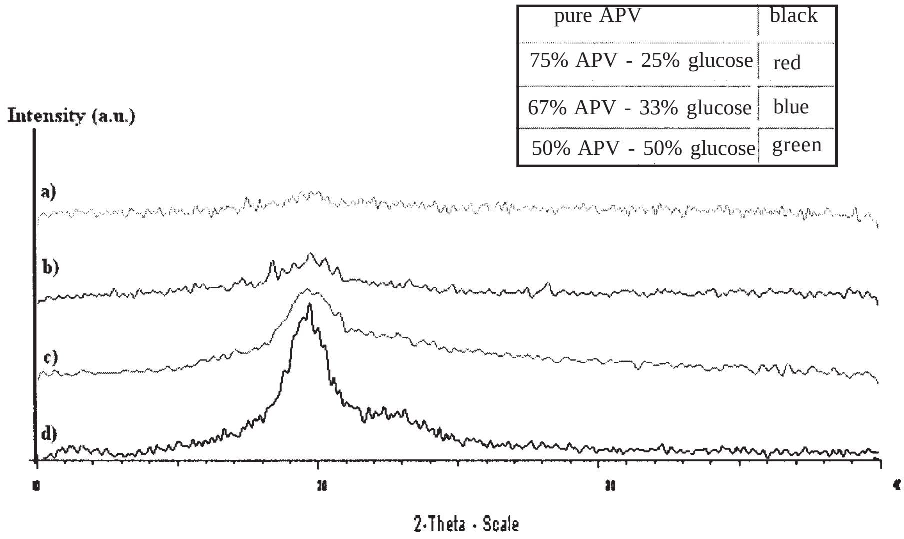


Fig. 5. XRD results

Conclusions

This study presents the influence of glucose on PVA films. The AFM results demonstrate the increasing of RMS with increasing of glucose percent on PVA foils. From FTIR and XRD measurements, the crystallinity of PVA degree was found to be lower at higher glucose percent. This can be attributed to the sample preparation as well, PVA recrystallized in a low-ordering form compared to the initial one.

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